

INFLUENCE OF CYCLIC CONDITIONING ON THE HYDROTHERMAL STABILITY OF LEATHER*

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ABSTRACT

The effect of cycling leather between various conditions of wetness and dryness was investigated. By means of Differential Thermal Analysis (DTA), it was shown that the shrinkage or transition temperature of leather is decreased in a relatively short time under the conditions employed. The decrease in shrinkage temperature was found to be dependent on type of tannage employed. Higher drying temperatures also accelerated this decrease. Subsequent exposure of conditioned specimens to 100 percent R.H. brought about a partial recovery of the loss in shrinkage temperature.



INTRODUCTION

While investigating the hydrothermal shrinkage temperatures of leather using differential thermal analysis (DTA), it was noted that many leathers exhibited a marked decrease in shrinkage temperature with time when stored under ordinary laboratory conditions. Some leathers were found to decrease as much as 30°C. over an extended period of time. This decrease in the shrinkage temperature of leathers on storage has been reported by other researchers (1). These losses in shrinkage temperature raised the question as to what conditions produce and/or accelerate thermal changes. Could it be due to the constant exchange of moisture that readily takes place in leather under normal laboratory conditions of humidity and temperature, and if so could it be accelerated by a somewhat greater variation in conditioning?

Certainly under normal conditions of wear the amount of water associated with leather varies from day to day depending upon such conditions as temperature, humidity, etc. Previously (2) we had shown that water is bound within the leather-tannage complex with various degrees of tenacity. If a change in the

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collagen structure occurs as a result of the loss or gain of bound water, then even under relatively mild cyclic conditioning the hydrothermal stability should change. This preliminary report shows the effects of time, temperature, and humidity on the shrinkage temperature of a variety of commercial leathers. Differential thermal analysis was employed for making the measurements.

EXPERIMENTAL

Materials.—Seven leathers with a variety of tannages and one untanned acetone dehydrated cowhide were selected for this study. The leathers represent a cross section of commercially available leather and were purchased immediately prior to the study undertaken and should represent relatively recently tanned leathers. The following side leather tannages were employed:

1. Chrome-chrome glutaraldehyde retan-finished
2. Straight chrome-unfinished (in the crust)
3. Chrome-vegetable retan unfinished (in the crust)
4. Chrome-vegetable retan finished
5. Chrome-chrome retan unfinished (in the crust)
6. Chrome-chrome retan finished
7. Chrome-vegetable glutaraldehyde-retan unfinished (in the crust)
8. Acetone dehydrated cowhide

Sampling.—All leathers received were stored for at least two days at 50 percent R.H. and 23°C. (73°F.) prior to sampling. About twelve samples 25mm x 5 mm were cut from each side of leather and were taken from the butt-backbone area. They were then exposed to various cyclic conditions of wetness and dryness which will be described later. At the end of each cyclic period samples 3 mm x 5 mm were removed for the shrinkage temperature measurement. Samples were wetted with water under vacuum for three minutes prior to shrinkage temperature measurement.

Instrumentation.—The shrinkage temperature measurements were made with a du Pont 900 Thermal Analyzer.† This instrument gives a thermograph having a pronounced minimum peak which reflects the shrinkage of leather (3). Since the peak temperature can be determined with the highest precision, it was used for comparative purposes and is referred to as shrinkage temperature throughout this report. A previous report (4) has shown that temperatures determined by DTA correlate very well with shrinkage temperatures measured by conventional means. Shrinkage temperatures were determined in a pressure cell (5), operated at 40 psi, as the leathers initially had shrink temperatures over 100°C. Measurements were made in excess water at a 10°C. per minute heating rate. Each leather was run in duplicate producing shrinkage temperatures which agreed to within + 1°C.

†The mention of commercial products is intended for your convenience and is in no way to be construed as an endorsement by the U. S. Department of Agriculture.

The weight measurements for moisture content were made by weighing the ten or twelve samples before and after each cyclic period minus the pieces removed for DTA measurement. These data produced percent moistures which agreed within ± 1 percent.

RESULTS

Effect of Various Cyclic Conditions.—Each leather was exposed to three different cyclic conditions. A complete cycle was arbitrarily set to extend for a period of one week. A total of nine cycles was used. It took approximately two months to complete the entire tests. Figure 1 shows the effect of three cyclic

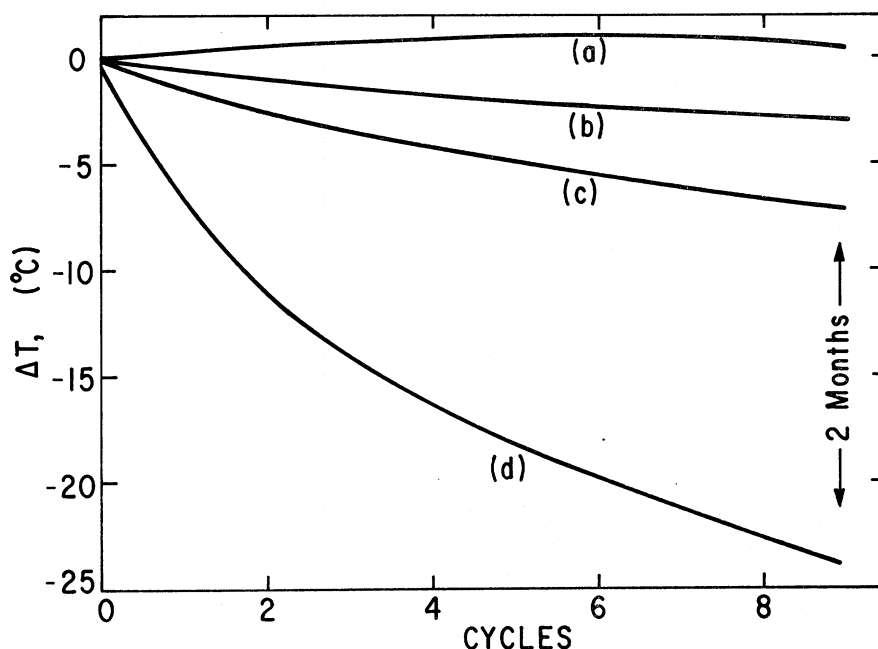


FIGURE 1.—Change in Shrinkage Temperature (ΔT) as a Function of the Number of Conditioning Cycles. (a) Control stored at 50% R.H. and 23°C. (73°F.); (b) one cycle: exposed 3 days to 23% R.H. and 23°C. and 4 days at 72% R.H. at 23°C.; (c) one cycle: dried 18 hours under vacuum at 23°C. and exposed 6 days to 50% R.H. and 23°C.; (d) one cycle: dried 18 hours under vacuum at 65°C. (149°F.) and exposed 6 days to 50% R.H. and 23°C.

conditions on a chrome-chrome glutaraldehyde retan finished leather. Plotted is shrinkage temperature change versus the number of cycles. The top curve, a, shows the data obtained on the unaged leather specimens which were held at 50 percent R.H. and 23°C. (73°F.) for two months and checked for shrinkage temperature periodically. During this period there was little or no detectable change in shrinkage temperature. The next curve, b, is for a cyclic condition of three days at 23 percent R.H. with a recovery of four days at 72 percent

R.H. while maintaining the temperature at 23°C. This condition caused a small but steady drop in shrinkage temperature which corresponded to about a 5°C. decrease after the ninth cycle. The third curve, c, represents the result obtained for a somewhat more severe cyclic conditioning, eighteen hours vacuum drying at 23°C. and six day equilibration at 50 percent R.H. and 23°C. This conditioning caused a more rapid decrease in shrinkage temperature which amounted to about an 11°C. decrease after the ninth cycle. Finally specimens were cycled between eighteen hours vacuum drying at 65°C. (149°F.) and six days recovery at 50 percent R.H. and 23°C. As shown in the bottom curve, d, the shrinkage temperature falls off rapidly in the first few cycles, with a total decrease of about 24°C. after the ninth cycle. Exposure of the original leathers to continuous drying in a vacuum oven at 65°C. for an equivalent time to that required for nine cycles showed only a 6°C. loss. These data indicate that moisture loss and subsequent regain by the leather produces a decrease in shrinkage temperature. Also the addition of heat during drying has a most pronounced effect.

The other six leathers investigated were subjected to these same conditions. Similar changes were observed to take place for the three cyclic conditions employed. Since the most severe conditions used gave the most accelerated deterioration to the hydrothermal stability, only the data from these conditions will be reported.

Shrinkage Temperature Changes for Various Leathers.—Figure 2 shows the shrinkage temperature for a straight chrome tanned unfinished leather (in the crust). Plotted is shrinkage temperature versus number of cycles. The top curve, a, is the control or uncycled leather which showed little or no change in shrinkage temperature at the end of two months at 50 percent R.H. and 23°C. The lower curve, b, shows the results obtained for the most severe cyclic condition used. The shrinkage temperature drops rapidly from 105°C. for about four cycles and then decreases somewhat more slowly to a value of 82°C. after nine cycles. This corresponds to a total decrease of about 23°C. in shrinkage temperature.

Shown in Figure 3 is the loss of shrinkage temperature as a function of the number of cycles of conditioning for four leathers and an acetone dehydrated cowhide. The top curve, a, is for untanned cowhide which shows a loss of only 8°C. at the end of the ninth cycle. The next two curves, b and c, are for chrome-chrome retan leathers. The upper curve, b, is for the finished leather and the other one, c, is for the unfinished leather. As can be seen, the unfinished leather shows an 18°C. loss while the finished leather lost only 15°C. at the end of the test, indicating that finishing tends to retard hydrothermal deterioration. This is further demonstrated by the lower two curves, d and e, which were obtained from a chrome-vegetable retan leather. The upper curve, d, is for the finished leather and the lower one, e, is for the unfinished leather. The shrinkage temperature of the finished leather decreased more slowly than the unfinished leather.

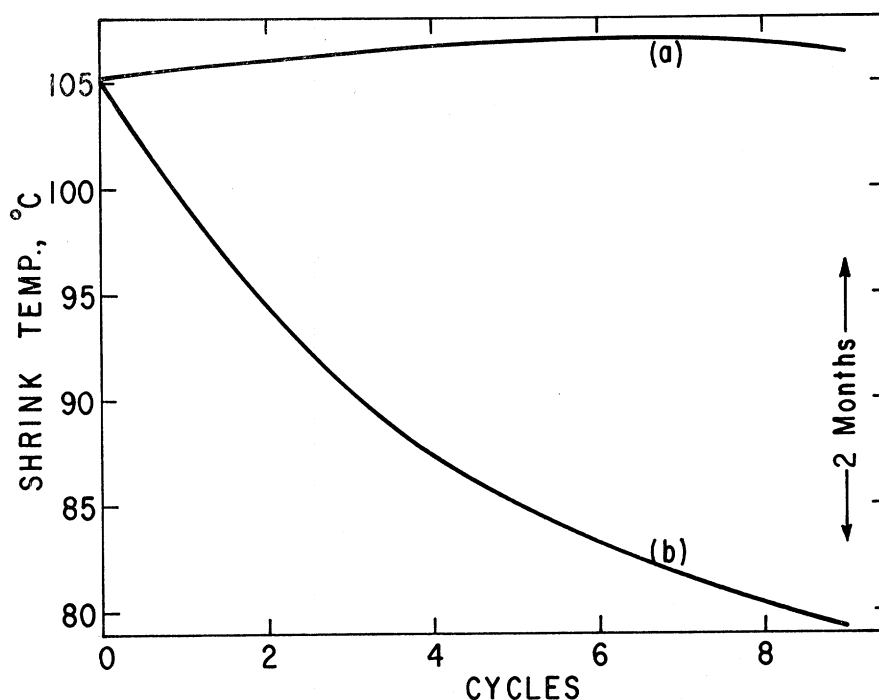


FIGURE 2.—Shrinkage Temperature Versus the Number of Conditioning Cycles. (a) Control stored at 50% R.H. and 23°C.; (b) one cycle: dried 18 hours under vacuum at 65°C. and exposed 6 days at 50% R.H. at 23°C.

for about four or five cycles, but it did not level off as the lower curve did. However, it reached the same loss in shrinkage temperature as the unfinished leather after eight cycles were completed.

The other three leathers investigated fell in between the chrome-chrome retan and the chrome-vegetable retan. The chrome-chrome retan showed the greatest stability to hydrothermal deterioration whereas the chrome-vegetable retan showed the poorest stability under the conditions investigated. This is further illustrated in Table I which summarizes the shrinkage temperature data. The leathers are listed according to decreasing loss in shrinkage temperature. As can be seen, the chrome-vegetable retan has the greatest loss, 31°C. The straight chrome and the chrome-chrome glutaraldehyde retan follow with a loss of 23°C. These are followed closely by the chrome-vegetable glutaraldehyde retan with a 21°C. loss. The chrome-chrome retans are next with losses of 18°C. and 15°C. The chrome-chrome retans show the lowest deterioration of the tanned materials. The acetone dehydrated cowhide showed the least change of any material studied, a loss of 8°C. These results indicate that the loss and subsequent regain of moisture by leather produces a decrease in shrinkage temperature which is dependent on the tannage and finishing of the leather.

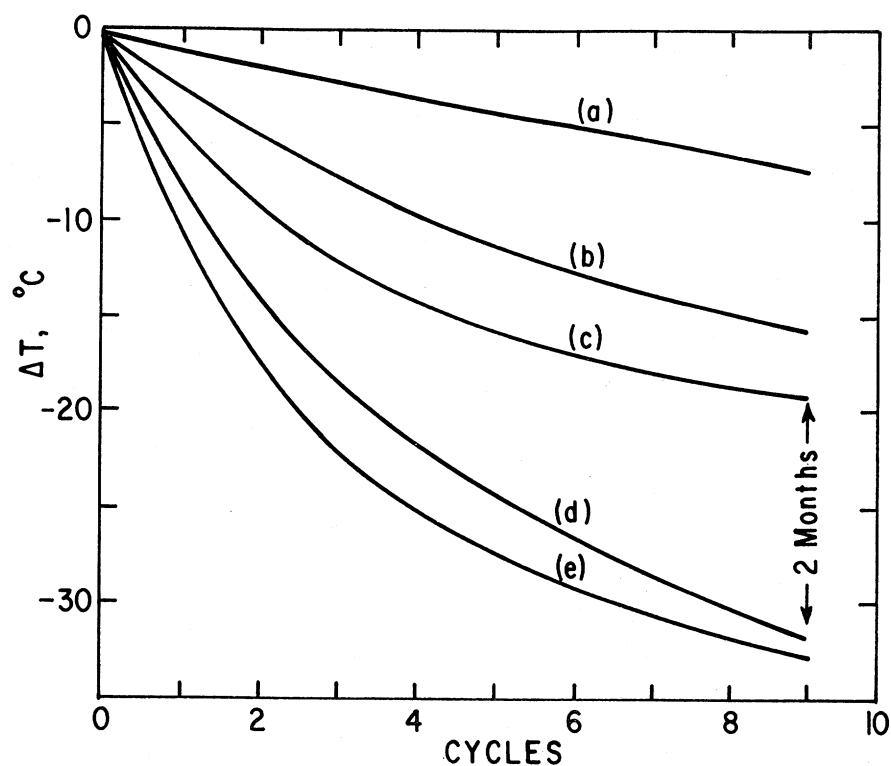


FIGURE 3.—Change in Shrinkage Temperature (ΔT) Versus Number of Conditioning Cycles for Various Leathers. (a) Untanned cowhide; (b) chrome-chrome retan finished; (c) chrome-vegetable retan finished; (d) chrome-vegetable retan finished; (e) chrome-vegetable retan unfinished (one cycle: dried 18 hours under vacuum at 65°C. and exposed 6 days to 50% R.H. at 23°C.).

TABLE I
EFFECT OF CYCLIC CONDITIONING ON SHRINKAGE TEMPERATURE^a

Leathers	Original Shrinkage Temp. (°C.)	9th Cycle Shrinkage Temp. (°C.)	Loss In Shrinkage Temp. (°C.)
1. Chrome-vegetable retan unfinished	111	80	31
2. Chrome-vegetable retan finished	109	79	30
3. Chrome — unfinished	105	82	23
4. Chrome-chrome glutaraldehyde retan finished	108	85	23
5. Chrome-vegetable glutaraldehyde retan unfinished	103	82	21
6. Chrome-chrome retan unfinished	103	85	18
7. Chrome-chrome retan finished	103	88	15
8. Acetone dehydrated cowhide	64	56	8

^aConditioning: 18 hr. vacuum drying at 65°C. (149°F.) and 6 days recovery at 50% R.H. and 23°C. (73°F.).

Effect of Cyclic Conditioning on DTA Peak.—It was noted that the peak areas were also decreasing with cyclic conditioning. Peak area is a measure of the energy required to produce a transition. A quantitative evaluation of these areas was not possible since our DTA test samples were not weighed; nevertheless, qualitative information was obtained from the curves. At the end of the nine cycles, the leathers lost from 50 to 95 percent of their ability to produce a peak. The cowhide lost only about 45 percent of its ability to produce a peak. There appears to be a direct correlation between shrinkage temperature change and peak area change; that is, the leathers showing the greatest loss in shrinkage temperature exhibited the greatest loss in peak area and the leathers having the lowest loss of temperature had the smallest change in peak area. In addition, the rate of decrease of peak area followed essentially the same pattern as the decrease in shrinkage temperature.

These results show that less energy is required for the transition from the helix-to-coil configuration of the collagen molecule after conditioning. This would indicate that the basic structure of the system has been modified by the relatively mild treatment to which it had been subjected. The fact that the untanned skin showed little change indicates that the tanning agent plays a major role in the reduced energy requirements. Was the structure permanently modified? To answer this question in part, the samples were then conditioned at 50 and 100 percent relative humidity to determine if a partial recovery could be attained.

Effect of Humidity on Cyclic Conditioned Samples

(1) *50 Percent R.H. and 23°C.*—After the ninth cycle some of the samples were left to recover at 50 percent R.H. and 23°C. At the end of 50 days equilibration, the specimens were tested. The shrinkage temperatures and the DTA peak areas were the same as they were after the ninth cycle, indicating that no great change had taken place.

(2) *100 Percent R.H. and 23°C.*—Some of the cycled samples were equilibrated in a desiccator at 100 percent R.H. and 23°C. Samples were removed periodically and tested over a period of 50 days. Unlike those equilibrated at 50 percent R.H., the samples equilibrated at 100 percent R.H. began to show a change in shrinkage temperature almost immediately. The shrinkage temperatures of the cyclic conditioned specimens, before and after equilibration at 100 percent R.H. for 50 days, are shown in Table II. Most of the leathers recovered about 10°C. The only leather that failed to recover this amount was the unfinished chrome-vegetable retan which recovered only 3°C. The untanned cowhide also showed little or no recovery, only 1°C.; however, its original total loss was only 8°C. The major part of this recovery was achieved within four days after conditioning at 100 percent R.H. The leathers recovered about 50 percent of their original shrinkage temperature loss, except for the chrome-vegetable retans which recovered only 10 to 30 percent.

TABLE II
EFFECT OF EQUILIBRATION AT 100% R.H. ON THE
SHRINKAGE TEMPERATURE OF CONDITIONED SAMPLES

Leathers	Shrinkage Temp. (°C.) (Cycled) ^a	Shrinkage Temp. (°C.) (100% R.H.) ^b	Increase In Shrinkage Temp. (°C.)
1. Chrome-vegetable retan unfinished	80	83	3
2. Chrome-vegetable retan finished	79	89	10
3. Chrome — unfinished	82	93	11
4. Chrome-chrome glutaraldehyde retan finished	85	95	10
5. Chrome-vegetable glutaraldehyde retan unfinished	82	90	8
6. Chrome-chrome retan unfinished	85	96	11
7. Chrome-chrome retan finished	88	99	11
8. Acetone dehydrated cowhide	56	57	1

^aConditioning: 9 cycles.

^bConditioning: 9 cycles plus 50 days at 100% R.H.

Not only did the shrinkage temperature recover with equilibration at 100 percent R.H. but the DTA peak areas also recovered. This DTA peak area recovery was fairly rapid with a return to within 50 percent of the original area after four days at 100 percent R.H. After 50 days at 100 percent R.H., the recovery was about 70 percent. The chrome-vegetable retans recovered the least amount of peak area of the seven leathers studied, just as they recovered the least amount of shrink temperature loss.

The partial recovery of the original transition temperature and the peak area show that the structure which was modified on cyclic conditioning is reformed at least in part. Apparently the change produced on cyclic conditioning is partially reversible. Why doesn't the structure re-form on soaking in water for a DTA run? The re-forming of the structure is time-dependent in the presence of moisture. It might have recovered at 50 percent R.H. providing a sufficient amount of time had been allotted for equilibration. However, it may need a certain level of water content before sufficient mobility of the basic structure is reached.

If moisture plays a role in the modification of the structure during cyclic conditioning, then a study of the amount of moisture retained by the specimens might throw some additional light on the subject.

Effect of Cyclic Conditioning on Moisture Content.—The percent moisture exchange for each cyclic period of the most severe conditioning was observed. The weight before and after each cyclic period was measured and the percent moisture based on sample dry weight was calculated. Figure 4 shows these data plotted for each cyclic period.

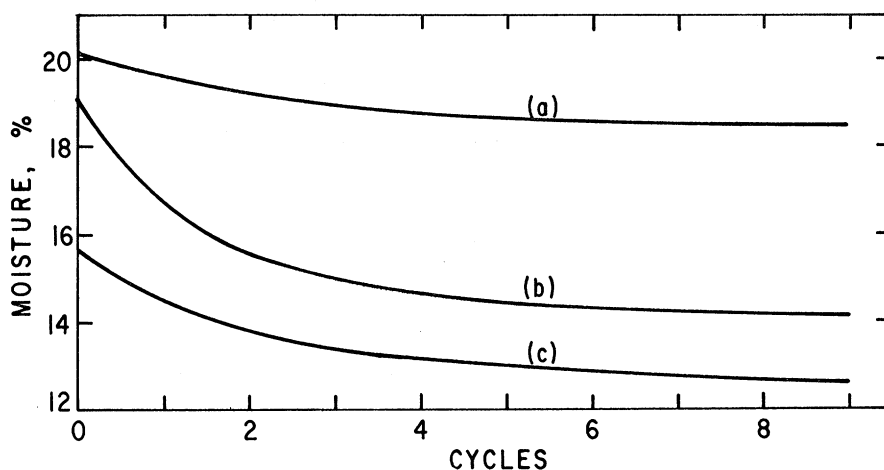


FIGURE 4.—Moisture Content as a Function of the Number of Conditioning Cycles. (a) Untanned cowhide; (b) straight chrome tan unfinished; (c) chrome-vegetable retan unfinished. (one cycle)

The bottom curve, c, is the unfinished chrome-vegetable retan and the middle curve, b, is the unfinished chrome tannage. Data for the other five leathers investigated lay between these two curves. The top curve, a, is the untanned cowhide. As shown, the chrome tannage (middle curve) based on the first drying cycle contained about 19 percent moisture. The moisture content decreases rapidly for the first few cycles to about 16 percent moisture and then more slowly to about 14 percent when the ninth cycle was reached. This corresponds to a decrease of five percent in moisture content from that which was held originally. The chrome-vegetable retan held 16 percent originally. It fell to about 14 percent in the first few cycles and then slowly decreased to about 13 percent when the ninth cycle was reached. This corresponds to a decrease of three percent in moisture content over that held originally. The untanned cowhide held 20 percent moisture originally, dropped to 19 percent in the first few cycles, and only decreased very slightly thereafter. All cycled samples were subsequently conditioned at 50 percent R.H. At the end of 50 days at these conditions, there was no recovery of the lost moisture. The moisture loss as a function of the number of cycles shows the same pattern as was seen with the shrink temperatures. There is a rapid change for the first few cycles and then a slow but steady decrease with further cycling.

The data show that there is a continuously decreasing amount of moisture regain with each conditioning cycle. The ability of the conditioned leather to take up moisture at 50 percent R.H. is reduced. This indicates that the number of sites available for sorbing water is decreasing as the structure is rearranging. The ability of the conditioned leathers to take up moisture can be regained by equilibration at 100 percent R.H., indicating an opening up of the molecular structure.

DISCUSSION

Structurally, what happened to the collagen-tannin system under the conditions investigated? Were bonds broken? If they were, what type of bond was broken — covalent, ionic, dipolar, or hydrogen? Are they inter-molecular or intra-molecular or both? If covalent bonds were the only ones broken, then essentially no recovery in shrinkage temperature or peak area should have been observed. On the other hand, if ionic, dipolar, or hydrogen bonds were involved, an almost complete recovery should have been observed if only slight structural rearrangement had taken place. Since only partial recovery of the shrinkage temperature was observed, it is indicated that some covalent linkages were broken and that the structural rearrangement produced was small. A relatively small movement of molecular groups within the system would greatly reduce the number of interactions, thereby decreasing the amount of energy required for shrinkage. However, if such a rearranged molecular system, which is restricted in its mobility, were provided with the proper environment, the original structure could be realized. Water molecules given sufficient time are able to penetrate into the molecular structure, giving mobility to the various groups involved, and the original structure is re-formed.

The results given in this paper further emphasize the great complexity of leather on the molecular level. Much more information along basic lines of investigation is needed before we can hope to understand and explain the behavior of leather.

CONCLUSIONS

Our results show:

- (1) Cyclic conditioning of leather, even under relatively mild conditions of temperature and humidity, produces a substantial decrease in hydrothermal stability in a relatively short time.
- (2) Increasing the temperature of drying produces a greater total decrease and an accelerated rate of decrease.
- (3) The decrease in hydrothermal stability observed is partially recoverable providing a sufficient amount of water is available and time is allowed for equilibrium.
- (4) Untanned skin shows a much smaller change as compared with that of tanned skins.

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DISCUSSION

MR. MEO: This paper will be discussed by Malcolm Battles of A. C. Lawrence Leather Company.

MR. BATTLES: I should like to thank Mr. Palm for a very interesting paper and one which points out something that I think many of us have observed in practice, where we notice a drop in shrinkage temperature with the aging of leather. In our own experience we have occasionally noticed that this is not accompanied by a change in the physical properties.

To refresh the memories of some of us here, Bill, will you tell us how the shrinkage temperature measured by the DTA relates to the Theis shrinkage temperature measurement?

MR. PALM: Well, as far as we know this peak that we obtain from our shrinkage temperature measurement is probably a degree or two higher than you would obtain on the Theis meter. The Theis measurement depends on the amount of weight that you apply to the sample. If it is a heavy weight the shrinkage temperature would possibly agree with the peak temperature; with a lower weight it would probably fall on the midpoint of the down slope or compare with our onset temperature. In other data that we have, it was found that a ten percent shrinkage corresponds more nearly to the peak temperature and a five percent shrinkage would fall somewhere on the midslope, that is, on the midpoint of the downslope of the curve or at the onset.

MR. BATTLES: Did you have an opportunity to take any of these aged samples and soak them in water to see what the recovery in shrinkage temperature would be after soaking?

MR. PALM: Yes, we took one of the aged leathers and soaked it in water. After the first two hours of soaking we began to see a slight increase in the shrinkage temperature, maybe about one or two degrees. We left it in overnight and by the next day we recovered about four or five degrees. In other words, it was approaching that which was obtained when we had exposed them to the one hundred percent R.H.

MR. BATTLES: Are there any questions from the floor?

A VOICE: Have you run any physical tests on the leathers that you were working with and related these to the cyclic conditions?

MR. PALM: No, we didn't have large enough samples which had been submitted to the cyclic conditions. About all I can say is, that from appearance we couldn't see any difference. We do not have any physical measurements to show it.

DR. PRENTISS (Rohm and Haas): I know that your discussion here relates to cycling from low humidity back to normal humidity, Bill, but what happens if you go to the other extreme? That is, you go from a high humidity condition back to normal. Have you studied this?

MR. PALM: We haven't done very much in that line but we have exposed some samples to 100 percent humidity, just for a few cycles and it appears that we get an increase in temperature, but we haven't carried these far enough to know where it will go after that.

MR. BATTLES: Are there any further questions?

MR. HOPKINS (Eastern Regional Research Lab.): Bill, did you say that finishing was beneficial?

MR. PALM: In most cases the finished samples showed a smaller decrease in temperature than the unfinished materials.

MR. HOPKINS: Well, I was just wondering was there a corresponding moisture loss there too, did they lose a lot more moisture than the other samples?

MR. PALM: Since the moisture percentages are pretty small, the differences might have been only one or two percent. It's hard to decide whether the finishing affected that or not.

MR. HOPKINS: In other words, finishing does seem to help, doesn't it?

MR. PALM: It definitely helped as far as minimizing the loss in shrinkage temperature, but as regards to moisture I couldn't be sure.

MR. HOPKINS: Thank you.

MR. BATTLES: Any further questions?

BRUCE SHARP (Ohio Leather Co.): Did you mention what kind of finish you had on the leather, and if you had different kinds, what kind.

MR. PALM: No, I didn't mention the type of finishing. They were standard production leathers, but I don't know just what the finishes were. For the par-

ticular tannages we worked with, the unfinished and the finished leathers were of the same tannage.

DR. SELIGSBERGER: With chrome-vegetable retan leather, was it stuffed leather?

MR. PALM: No, as far as I know, it wasn't.

MR. BATTLES: Any further questions? Then again I want to thank Mr. Palm for his very interesting paper.
